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Chalcopyrite Semimagnetic Semiconductors: from Nanocomposite to Homogeneous Material

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Abstract:

Currently, complex ferromagnetic semiconductor systems are of significant interest due to their potential applicability in spintronics. A key feature in order to use semiconductor materials in spintronics is the presence of room temperature ferromagnetism. This feature was recently observed and is intensively studied in several Mn-alloyed II-IV-V_2 group diluted magnetic semiconductor systems. The paper reviews the origin of room temperature ferromagnetism in II-IV-V_2 compounds. In view of our recent reports the room temperature ferromagnetism in Mn-alloyed chalcopyrite semiconductors with more than 5 molar % of Mn is due to the presence of MnAs clusters. The solubility of magnetic impurities in bulk II-IV-V_2 materials is of the order of a few percent, depending on the alloy composition. High values of the conducting hole - Mn ion exchange constant J_{pd} have significant value equal to 0.75 eV for $Zn_{0.997}Mn_{0.003}GeAs_2$. The sample quality has significant effect on the magnetotransport of the alloy. The magnetoresistance of the alloy change main physical mechanism from spin-disorder scattering and weak localization for homogeneous samples to cluster-related geometrical effect observed for nanocomposite samples. The magnetoresistance of the II-IV-V_2 alloys can be then tuned up to a few hundreds of percent via changes of the chemical composition of the alloy as well as a degree of disorder present in a material.

Keywords: *Semimagnetic-semiconductors; Magnetic-impurity-interactions, Exchange-interactions.*

1. Introduction

The practical applications of ferromagnetic semiconductors require materials with the Curie temperature, T_C, greater than room temperature. Most of the literature reports about the magnetic properties of diluted magnetic semiconductors (DMS) show the Curie temperature much lower than 300 K, which makes these compounds of a little use for practical applications.[1] The conventional, intensively studied and well understood ferromagnetic

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semiconductors based on III-V, II-VI, or IV-VI compounds are of a major importance but does not show room temperature ferromagnetism in homogeneous samples.[2,3] The lack of room temperature ferromagnetic semiconductor systems creates the need for the development of new compounds fulfilling practical application requirements. A few decades of mastering the technology of growth of classical homogeneous ferromagnetic semiconductors does not give perspectives to obtain the Curie temperatures higher than 200 K.[4] One of the ideas to solve the problem of semiconductor spintronics is to utilize inhomogeneous hybrid semiconductor/ferromagnetic cluster composite systems with the Curie temperature exceeding room temperature. Chalcopyrite semiconductors are perceived as an important class of materials since they offer several, potentially applicable properties. Chemically chalcopyrite compounds are ternary analogues of binary III-V materials. The tetragonal chalcopyrite crystal structure is similar to the zincblende structure. Thus, many of the II-IV-V_2 compounds are lattice matched to their III-V analogues,[5] making them compatible to existing commercial technology.[6,7] The chalcopyrite compounds can be an efficient sources of spin polarized photoelectrons due to the nondegenerate top of the valence band.[8] In addition, large nonlinear optical coefficients reported for example for $CdGeAs_2$ system and a direct energy gap at the Γ point of the Brillouin zone makes these materials suitable for applications in nonlinear optics.[9] Room temperature ferromagnetism was recently observed in several representatives of II-IV-V_2 chalcopyrite semiconductors.[10,11] There are several reports showing ferromagnetic alignment in $Cd_{1-x}Mn_xGeP_2$,[12] $Zn_{1-x}Mn_xSnAs_2$,[13] and Zn_{1-x} Mn_xGeP_2,[14,15] with the T_C equal to 320, 329 and 312 K, respectively. The existence of the pressure-induced metamagnetic states was also recently observed in $Cd_{1-x}Mn_xGeAs_2$ alloy.[16,17]

In the present paper we review the current progress in the understanding of the structural, electrical, and magnetic properties of the II-IV-V_2 DMS systems. Initially it was proposed that the magnetic order at room temperature in chalcopyrite DMS can be due to the itinerant carrier mediated interactions between Mn-ions.[18] The theoretical studies predict that the presence of antiferromagnetic state in $Cd_{1-x}Mn_xGeP_2$ is preferred.[19] The impurity induced ferromagnetism was also claimed to be responsible for the observed magnetic properties of Mn-doped chalcopyrite alloys.[20] Apart of the above possible explanations our recent extensive experimental studies revealed that the room temperature ferromagnetism with maximum T_C of about 367 K in Mn-alloyed $Zn_{1-x}Mn_xGeAs_2$ samples[21] is due to the presence of the MnAs clusters of different sizes and shapes. The physical properties of the nanocomposite II-IV-V_2 samples show interesting and possibly applicable magnetotransport properties such as: (i) negative magnetoresistance with maximum amplitudes of about -50 % observed for the $Zn_{1-x}Mn_xGeAs_2$ samples with $x \geq 0.078$ at $T < 10$ K and (ii) positive magnetoresistance with maximum amplitudes of about 500 % observed for $Cd_{1-x}Mn_xGeAs_2$ crystals observed for the samples with $x > 0.045$ at $T < 300$ K. The observed magnetoresistance effects are related to the presence of ferromagnetic MnAs clusters present in the semiconductor lattice. The homogeneous limit of alloying of $Cd_{1-x}Mn_xGeAs_2$ and $Zn_{1-x}Mn_xGeAs_2$ alloys indicate that the solubility limit of Mn ions inside the chalcopyrite lattice is around a few molar percent. The detailed studies of the magnetic properties of $Zn_{1-x}Mn_xGeAs_2$ samples show that the Mn-distribution is random in the cation sites of the host lattice only for the sample with the lowest Mn-content, $x = 0.003$. The samples with larger Mn-content show a high level of magnetic frustration. Nonzero Curie-Weiss temperature observed in all our samples indicates that weak ferromagnetic (for $x = 0.003$) or antiferromagnetic (for $x > 0.005$) interactions with $|\theta| < 3$ K are present in this system. The RKKY model, used to estimate the Mn-hole exchange integral J_{pd} for the $Zn_{0.997}Mn_{0.003}GeAs_2$ sample, allow to estimate the value of $J_{pd} = (0.75 \pm 0.09)$ eV. A significant value of J_{pd} gives perspectives for introduction of carrier mediated itinerant ferromagnetism in the homogeneous Mn-alloyed chalcopyrite alloys.

2. Room temperature ferromagnetism

In the following section the results explaining the room temperature ferromagnetism in the selected representatives of Mn-alloyed II-IV-V_2 chalcopyrite DMS are presented. A detailed characterization of the crystals is needed in order to experimentally prove the existence of ferromagnetic clusters. It is often difficult to prove the existence of nanosized clusters with the use of the straightforward methods. However, a detailed, state-of-the-art high resolution x-ray diffraction measurements (HRXRD) and precise data analysis is capable to detect the presence of nanometer-sized clusters.[23] As an example the diffraction patterns detected for the $Zn_{1-x}Mn_xGeAs_2$ crystals are presented in Fig. 1a. The HRXRD results showed that the addition of Mn to the alloy significantly decrease the crystal quality. For the low Mn-content sample with x = 0.053 the X-ray diffraction pattern showed the existence of two main phases. One was identified as a chalcopyrite phase with lattice parameters a = 5.664 ± 0.001 Å and c = 11.169 ± 0.005 Å, which points to a solid solution of Mn in $ZnGeAs_2$. The second phase can be described as a solid solution of Mn in the $Zn_2Ge_{11}As_4$ compound. The crystal structure of $Zn_2Ge_{11}As_4$ without Mn is cubic in the space group F-43m [JCPDS, 50-722] with lattice parameter a = 5.6531 Å. In the case of the ferromagnetic $Zn_{1-x}Mn_xGeAs_2$ samples with x > 0.07 the detailed indexing procedure shows the presence of MnAs precipitates. In addition to the main phase identified as tetragonal chalcopyrite structure the HRXRD results showed the presence of the hexagonal [JCPDS, 28-644] and orthorhombic [JCPDS, 72-1065] MnAs phases (See the inset to Fig. 1a). It clearly demonstrates that the solubility limit in case of these two samples was surpassed.

In order to investigate the origin of the observed ferromagnetism discovered in $Zn_{1-x}Mn_xGeAs_2$ samples with x > 0.078 the zero-field Nuclear Magnetic Resonance (NMR) measurements can be done. This technique seems to be ideal for our purposes due its sensitivity to the nanometric phase separation. NMR spin echo measurements of ^{55}Mn and ^{75}As were done at temperature T = 4.2 K (see Fig. 1b). The obtained NMR spectra are characterized by broad peaks near 210 and 240 MHz for all nanocomposite samples. Similar NMR spectra were also observed for $Cd_{1-x}Mn_xGeAs_2$ alloy.[24] The inset to Fig. 1b shows the NMR spectrum in a limited frequency range, obtained with higher frequency resolution in $Zn_{1-x}Mn_xGeAs_2$ sample (x = 0.078). The results indicate that no NMR intensity has been observed in the frequency range characteristic for Mn^{2+} ions in ferromagnetic state. It indicates that the magnetic properties of the alloy do now originate from the randomly distributed Mn ions. The obtained peaks in the NMR spectra can be readily attributed to the existence of ferromagnetic phase of MnAs. The ^{55}Mn and ^{75}As NMR peaks observed in this case have positions identical to the peaks attributed to MnAs located at 236.1 and 207.9 MHz, respectively.[25] The quadruple splitting of the ^{55}Mn and ^{75}As NMR spectra reported in the previous study[25] was not observed due to the random MnAs cluster orientation inside the highly disordered $Zn_{1-x}Mn_xGeAs_2$ crystals. The results show clearly the strong signal coming from MnAs phase in the $Zn_{1-x}Mn_xGeAs_2$ crystals.

Optical methods are often very helpful to determine the structural quality of the alloy. Among all the optical methods Raman spectroscopy is very sensitive method to detect the changes in the structure of the material. Recent studies devoted to the $Zn_{1-x}Mn_xGeAs_2$ alloy[27] (see Fig. 1c) show several features not observed with the other techniques. Narrow peaks in Fig. 1c correspond to phonons of $ZnGeAs_2$.[29] For the homogeneous samples with $x \leq 0.053$ most of the features in the Raman spectra are similar. The spectrum that stands out from others in Fig. 1c corresponds to the sample with the highest Mn content, x = 0.078. There exist only theoretical calculations of the position of MnAs phonons in the literature.[30,31] The modes for $Zn_{0.922}Mn_{0.078}GeAs_2$ sample present at a wavelength of about 170 cm^{-1} can be assigned to a group of modes residing from 165 to 177 cm^{-1}, which correspond to both hexagonal and orthorhombic MnAs phases. Moreover, the modes predicted for MnAs to be located at wavelengths equal to 241.6, 254.5, and 257.9 cm^{-1} preferably correspond to the

mode observed for $Zn_{0.922}Mn_{0.078}GeAs_2$ sample at 250 cm^{-1} from the spectrum presented in Fig. 1c. The observation of several peaks related to the MnAs phases in the $Zn_{0.922}Mn_{0.078}GeAs_2$ sample is a clear indication of the presence of magnetic clusters in the material.

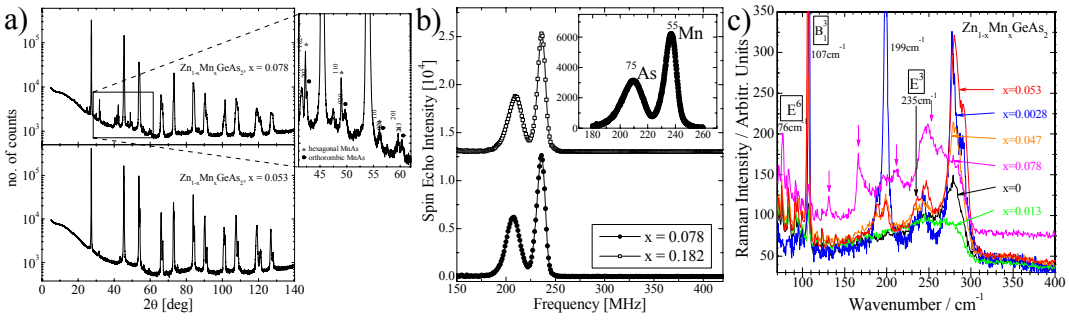

Fig. 1. Evidence for the presence of the magnetic MnAs inhomogeneities in the $Zn_{1-x}Mn_xGeAs_2$ crystals including (a) high resolution x-ray diffraction, (b) nuclear magnetic resonance data, and (c) Raman spectra obtained at room temperature. Reprinted with permission from L. Kilanski et al., J. Appl. Phys. 108, 073925 (2010). Copyright 2010, AIP Publishing LLC. Reprinted from Publication Journal of Alloys and Compounds, 548, M. Romčević et al., Optical properties and plasmon – Two different phonons coupling in $ZnGeAs_2$ + Mn, 33-37, Copyright (2013), with permission from Elsevier.

Recently, the appearance of ferromagnetic order was studied in detail for $Zn_{1-x}Mn_xGeAs_2$ and $Cd_{1-x}Mn_xGeAs_2$ alloys. Both compounds, for Mn-amount higher than a few molar percent show ferromagnetic order with the Curie temperature, T_C, as high as 367 K for $Zn_{1-x}Mn_xGeAs_2$ with 3.5 wt. % of Mn.[21,6] The structural characterization of the chalcopyrite alloys show that the room temperature ferromagnetism in Mn-doped chalcopyrite alloys is due to the presence of the MnAs clusters of different sizes and shapes. The Curie temperature of the chalcopyrite compounds show slight variations, depending on the geometrical and chemical properties of the MnAs clusters. However, it should be noted, that the determination of the T_C given by different authors differ and it is difficult to directly compare them. The Curie temperature of the $Zn_{1-x}Mn_xGeAs_2$ (see Refs. 22, 23) and $Cd_{1-x}Mn_xGeAs_2$ (Ref. 24) alloys show reliably determined changes by at least 10 K (see Fig. 2). The presented data for $Zn_{1-x}Mn_xGeAs_2$ alloy show that the solubility limit of Mn ions in the chalcopyrite lattice is as high as about 6 %. Above this quantity the magnetic order due to the presence of magnetic inhomogeneities are present. Slight changes of the T_C comes from the differences between the geometrical (cluster sizes and shapes) and structural (chemical composition and crystal structure) properties of the MnAs phases in each individual crystal. The values of the Curie temperatures are close to the values reported for the $Ga_{1-x}Mn_xAs$ samples containing MnAs clusters.[33] Moreover, the differences in parameters characterizing the clusters were proven to be responsible for the slight changes in the Curie temperature, T_C.[34]

The divergent behavior of the zero-field-cooled and field-cooled magnetization is a typical feature observed in nanocomposite chalcopyrite samples.[23] Such a feature is characteristic of the presence of a large magnetic disorder in the crystals. The magnetic disorder comes from large fraction of paired Mn ions. Antiferromagnetic pairing lowers the effective magnetic moment per magnetic ion and induces disorder into the system. It is also obvious that the charge state of the magnetic impurities inside the chalcopyrite lattice can differ from the high-spin-only ground state for Mn^{2+} with S = 5/2. This again induces the magnetic disorder in the crystals.

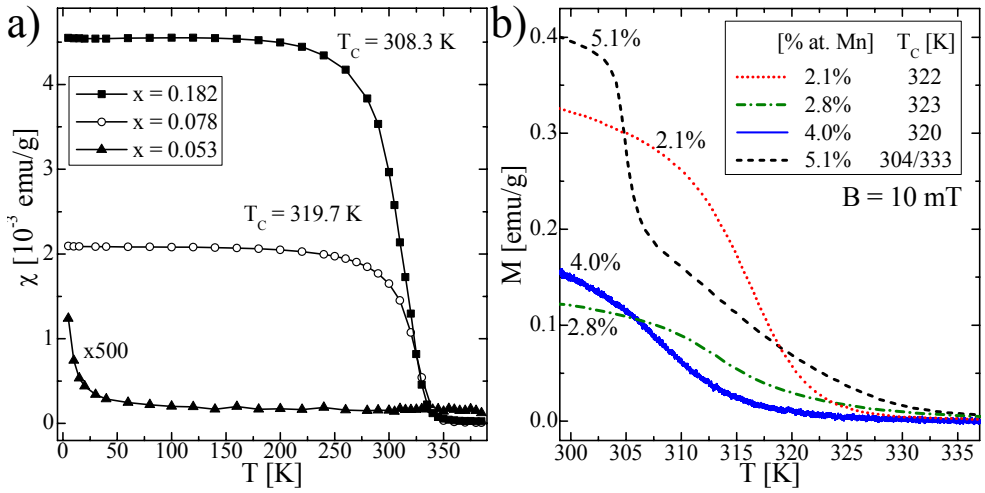

Fig. 2. The magnetic properties of Mn-alloyed II-IV-V_2 materials including: (a) the temperature dependence of the magnetic susceptibility for the $Zn_{1-x}Mn_xGeAs_2$ samples and (b) the temperature dependence of the magnetization for the $Zn_{1-x}Mn_xGeAs_2$ crystals. Reprinted with permission from L. Kilanski et al., J. Appl. Phys. 108, 073925 (2010). Copyright 2010, AIP Publishing LLC

The magnetotransport properties of the Mn-alloyed II-IV-V_2 samples show interesting magnetotransport properties related to the presence of the magnetic clusters. The magnetoresistance (MR) curves for $Zn_{1-x}Mn_xGeAs_2$ crystals containing MnAs clusters shows quadratic positive magnetoresistance at temperatures higher than 15 K, interpreted as cyclotron movement of charge carriers in a magnetic field. Below 15 K the presence of negative magnetoresistance in all the nanocomposite crystals can be observed (see Fig. 3a). The maximum amplitudes of the magnetoresistance of about -50 % were observed for the $Zn_{1-x}Mn_xGeAs_2$ samples with \$x\$\,\$\$≥\$\,\$0.078.[23]

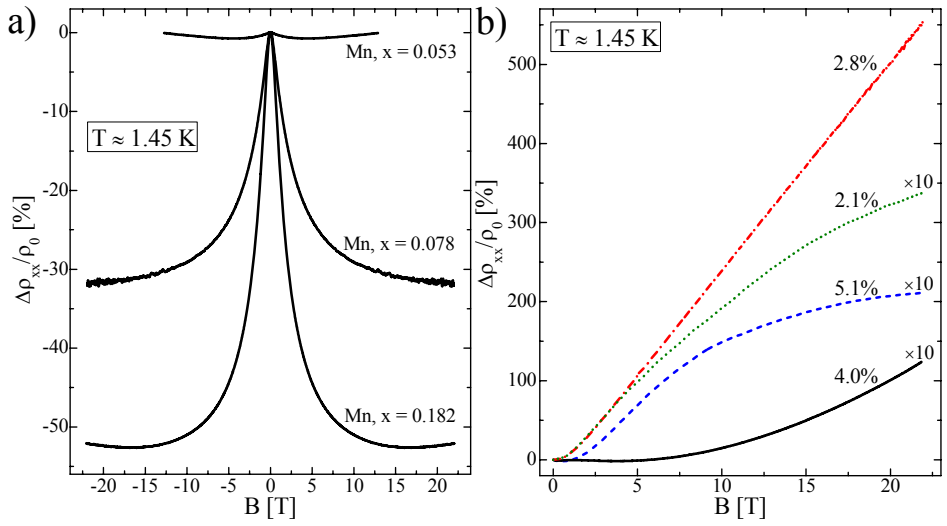

Fig. 3. Magnetoresistance curves observed at different temperatures in nanocomposite: (a) $Zn_{1-x}Mn_xGeAs_2$ and (b) $Cd_{1-x}Mn_xGeAs_2$ samples with different chemical composition. Reprinted with permission from L. Kilanski et al., J. Appl. Phys. 108, 073925 (2010). Copyright 2010, AIP Publishing LLC. Reprinted from Solid State Communications, 151, L. Kilanski et al., Colossal linear magnetoresistance in a $CdGeAs_2$:MnAs micro-composite ferromagnet, 870-873, Copyright (2011), with permission from Elsevier.

The negative magnetoresistance in the nanocomposite samples is be caused by the presence of metallic clusters of manganese arsenide. The tunneling of spin polarized carriers in the ferromagnetic granular media causes the negative magnetoresistance. This effect is known as giant magnetoresistance (GMR) and was observed in many granular materials exhibiting ferromagnetic ordering.[35,36]

The large positive magnetoresistance was observed recently in a number of inhomogeneous granular systems.[36-38] The linear positive magnetoresistance effects were reported to exist in the systems containing both magnetic impurities and the nonmagnetic materials. The large magnetoresistance effects are related to the fluctuations of the resistivity in the systems containing clusters randomly distributed in the material. It is believed that the large positive magnetoresistance observed in the chalcopyrite $Cd_{1-x}Mn_xGeAs_2$ crystals.[24] The highest value of the magnetoresistance was observed in the sample with 2.8 at. % of Mn and reached about 550\% at T = 1.5 K. The lack of correlation between the magnetic properties of the samples and the presence of the relation between the Hall mobility of the sample and the value of the magnetoresistance seem to confirm that the geometrical magnetoresistance is responsible for the observed colossal magnetoresistance. The reported effects has one of the highest observed amplitudes and persists with a large value around 250 % even at temperatures as high as 200 K. A significant magnetoresistance persisting at high temperatures is an important property related to the possible applications of chalcopyrite nanocomposite materials in spintronics.

3. Homogeneous distribution of magnetic ions

The solubility limit of the Mn ions inside the II-IV-V_2 bulk materials grown with the use of thermodynamical equilibrium techniques is much higher than in the bulk III-V materials. The paramagnetic response of the $Zn_{1-x}Mn_xGeAs_2$ alloy is observed for $x \leq 0.053$.[26,28] To our knowledge at the moment there exist no other reports showing homogeneous distribution of Mn ions in the chalcopyrite lattice. The inverse of the real part of the ac magnetic susceptibility $Re(\chi_{ac}(T))$ show the Curie-Weiss behavior only for the smallest Mn content, x = 0.003 (see Fig. 4a). For the higher x, a slight deviations from the Curie-Weiss law are visible indicating the presence of a significant fraction of the Mn-ions that are not randomly distributed in the semiconductor lattice.

The susceptibility data fitted with the modified Curie-Weiss law allowed the determination of the Mn-content dependence of the Curie-Weiss temperature, θ, and the effective Mn-content, $\bar{x}_{Mn}$ (see Fig. 4b). The results show that the Curie-Weiss temperature changed sign with an increase of the Mn content. It is a signature that the dominant magnetic interactions in this system changed from ferromagnetic at low composition x to antiferromagnetic for x between 0.003 and 0.014. Moreover with the increase of Mn in the alloy above x = 0.003, the amount of Mn not diluted randomly in the crystal increases. The amount of magnetically active Mn ions, $\bar{x}_{Mn}$, is close to the average Mn content, x, only for the case of the $Zn_{0.997}Mn_{0.003}GeAs_2$ sample with the lowest x. For all the crystals with $0.014 \geq x \geq 0.042$, the amount of magnetically active Mn ions remaining in the high spin-state with S = 5/2 does not exceed $\bar{x}_{Mn} = 0.0056 \pm 0.001$. It is also evident that the majority of Mn ions in $Zn_{1-x}Mn_xGeAs_2$ alloy with $x \geq 0.014$ do not substitute for Zn sites in the crystal lattice and therefore possess smaller net magnetic moment than Mn^{2+} or that a large fraction of Mn ions in these samples occupies interstitial sites of the crystal lattice, which promotes short range superexchange interactions leading to antiferromagnetic pairing of Mn ions and zero net magnetic moment of such pairs. The antiferromagnetic state of Mn ions with zero magnetic moment was shown to be energetically preferred for $Zn_{1-x}Mn_xGeAs_2$ alloy with x = 0.25 and

0.50.[20] It is therefore highly probable that the magnetic ions form antiferromagnetic states in this semiconductor matrix when the x value is higher than 0.25.

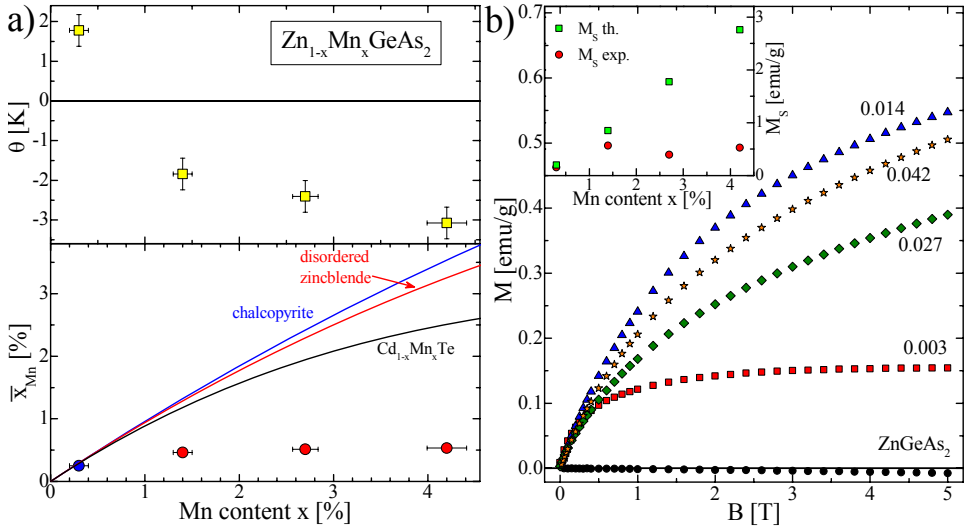

Fig. 4. The magnetic properties of the $Zn_{1-x}Mn_xGeAs_2$ crystals including (a) the Curie-Weiss temperature (upper figure) and the effective Mn-content $\bar{x}_{Mn}$ as a function of the Mn molar fraction x and (b) the magnetic field dependence of the magnetization M measured at T = 4.5 K and the saturation magnetization (inset to figure) fitted (red symbols) and calculated (yellow symbols) as a function of the Mn content, x. Reprinted with permission from L. Kilanski et al., J. Appl. Phys. 108, 073925 (2010). Copyright 2010, AIP Publishing LLC.

A high quality of the $Zn_{1-x}Mn_xGeAs_2$ alloy with x = 0.003 and Mn incorporation into cation sites inside the chalcopyrite lattice was confirmed by the electron paramagnetic resonance measurements. [28] The EPR results indicate the presence of thirty resonance lines - a pattern, characteristic of Mn^{2+} ions showing both fine and hyperfine structure components, due to electron spin S = 5/2 and nuclear spin I = 5/2, respectively. For such a sample it is then believed that the random distribution of Mn ions occurs. The magnetization curve observed for the chalcopyrite $Zn_{1-x}Mn_xGeAs_2$ sample with x = 0.003 shows a behavior characteristic of a paramagnet, i.e., the M(B) curve can be easily fitted with the use of Brillouin function (see Fig. 4b). Moreover, the saturation of the M(B) curve for the sample with x = 0.003 is reached at the magnetic field B ≈ 3 T (see the inset to Fig. 4b). It is a signature of a random Mn-distribution in the host lattice, and probably lack of significant antiferromagnetic Mn-pairing. The addition of a higher quantity of Mn to the alloy resulted in a different shape of the M(B) curve for our crystals with x > 0.01. For such a very diluted sample with x = 0.003 it was possible to calculate with rather large confidence the value of the Mn-ion - conducting hole exchange integral J_{pd}. The obtained values of the conducting hole - Mn ion exchange constant J_{pd} have significant value equal to 0.75 eV which creates possibility to develop homogeneous ferromagnetic semiconductor materials based on chalcopyrite materials.

The magnetoresistance of the low Mn-content samples show different origin than in the ferromagnetic samples.[26,28] For the nonmagnetic $ZnGeAs_2$ crystal MR is positive and is proportional to the square of the magnetic field in the entire temperature range (1.4...300 K). This effect can be associated with the classical magnetoresistance due to the orbital motion of carriers in a magnetic field. Moreover, in the $ZnGeAs_2$ sample at low temperatures, there are no other contributions to the MR, such as the weak localization (WL) of carriers on defect states.[39] The MR curves for selected $Zn_{1-x}Mn_xGeAs_2$ samples performed at several stabilized temperatures are presented in Fig. 5.

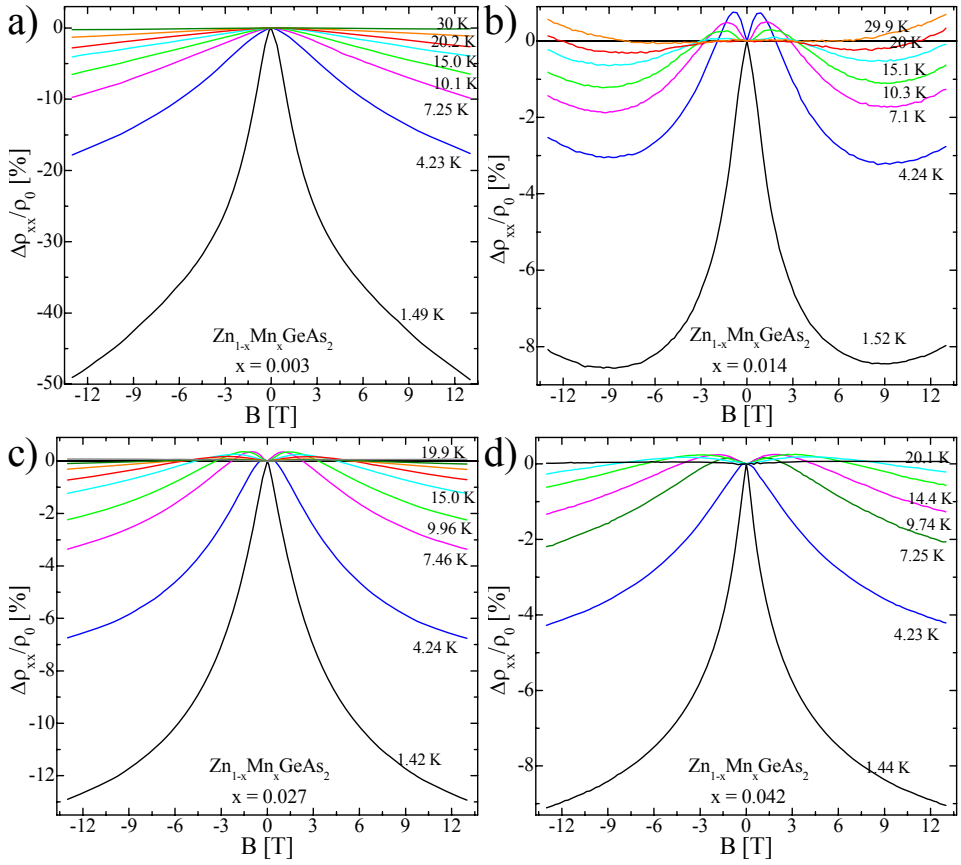

Fig. 5. The magnetoresistance curves obtained experimentally at different temperatures for $Zn_{1-x}Mn_xGeAs_2$ samples with different chemical composition. Reprinted with permission from L. Kilanski et al., J. Appl. Phys. 108, 073925 (2010). Copyright 2010, AIP Publishing LLC.Fig. 1.

The results indicate that the addition of a small quantity (x = 0.003) of Mn to the $Zn_{1-x}Mn_xGeAs_2$ alloy results in a significant change of the MR behavior with respect to the nonmagnetic $ZnGeAs_2$ sample. The results show a negative MR for the $Zn_{1-x}Mn_xGeAs_2$ samples, present at temperatures lower than 30 K. MR curves for the $Zn_{1-x}Mn_xGeAs_2$ samples with $x \leq 0.042$ studied in Ref. 28 have a different shape and an amplitude of the order of magnitude higher than that studied in Ref. 26 ($Zn_{0.947}Mn_{0.053}GeAs_2$ sample of similar concentration and mobility of carriers at T = 1.4 K). It is therefore clear that in the case of currently studied samples, the magnetoresistance should be associated with a different mechanism than the spin-disorder scattering process claimed to be the leading mechanism of MR in $Zn_{0.947}Mn_{0.053}GeAs_2$. The negative MR in paramagnetic $Zn_{1-x}Mn_xGeAs_2$ samples is caused by the WL in the presence of spin-orbit interaction and magnetic impurity scattering.[40] The samples show strong localization and the theories of MR predict a presence of both positive (at low magnetic fields) and negative MR (at higher fields) due to WL phenomena. The MR in the paramagnetic $Zn_{1-x}Mn_xGeAs_2$ samples decreases as a function of the increasing average Mn content, x. Thus, the observed MR cannot related to a magnetic impurity scattering mechanism that would lead to MR proportional to the amount of magnetic impurities in the crystal. WL phenomena is destroyed by the presence of magnetic impurities in the material. The destruction of the WL by the presence of an increasing number of magnetic impurities in the crystals explains the observed MR in the $Zn_{1-x}Mn_xGeAs_2$ samples with $x \leq 0.043$.

4. Summary

We presented the current state-of-the-art in the field of development of complex ferromagnetic semiconductor systems. These materials are of significant interest due to their potential applicability in spintronics. We reviewed the current understanding of the origin of room temperature ferromagnetism in II-IV-V_2 diluted magnetic semiconductors. In view of recent reports it seems that the room temperature ferromagnetism in Mn-alloyed chalcopyrite semiconductors is due to the presence of MnAs clusters of different sizes. The possibilities of random distribution of magnetic ions inside the II-IV-V_2 crystals are also reviewed. The solubility of magnetic impurities in II-IV-V_2 materials is of the order of a few percent, depending on the alloy composition. High values of the conducting hole - Mn ion exchange constant J_{pd} have significant value equal to 0.75 eV for $Zn_{1-x}Mn_xGeAs_2$ which creates possibility to develop homogeneous ferromagnetic semiconductor materials based on chalcopyrite materials. The sample quality have significant effect on the magnetotransport of the alloy. The magnetoresistance of the alloy change main physical mechanism from spin-disorder scattering and weak localization for homogeneous samples to cluster-related geometrical effect observed for nanocomposite samples.

Acknowledgments

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Садржај: *У садашње време комплексни феромагнетни полупроводнички системи су од великог интереса због њихове могуће примене у спинтроници. Главна особина која издваја полупроводнике као погодне материјале за примену у спинтроници је присуство феромагнтизма на собној температури. Ова особина је недавно примећена и интезивно проучавана у неколико система разблажених магнетних полупроводника из групе II-IV-V_2 допираних манганом. У овом раду размотрено је порекло феромагнетизма на собној температури у II-IV-V_2 једињењима. Имајући у виду наше скорашње радове, у халкопиритним полупроводницима допираним са више од 5 моларних % мангана феромагнетизам на собној температури се јавља услед присуства кластера MnAs. Растворљивост магнетних примеса у чврстим II-IV-V_2 материјалима је реда неколико процената, зависно од састава једињења. Високе вредности проводна шупљина – Mn јон изменске константе J_{pd} су значајне и износе 0.75 eV за $Zn_{0.997}Mn_{0.003}GeAs_2$. Квалитет узорка има значајан утицај на магнетотранспорт легуре. Магнетоотпорност легуре мења основни физички механизам од спин-неуређеног расејања и слабе локализације код хомогених узорака, у геометријски ефекат повезан са кластерима који је регистрован код нанокомпозитних узорака. Магнетоотпорност код II-IV-V_2 једињења тако може бити повећана за неколико стотина процената путем мењања хемијског састава једињења као и степена неуређености присутне у материјалу.*

Кључне речи: *Полумагнетни полупроводници, интеракције магнетне примесе, изменска интеракција.*